The only values available for comparison with these for ions in moist air are those of Zeleny, who obtained values for vp/X ranging from 960 to 1080, but his work was done with values of X and of p very different from those considered here, and the experiments of Przibram, who obtained for vp/X the values 1005 in moist air and 1160 in air partially dried by sulphuric acid.

On the Variation with Temperature of the Viscosities of the Gases of the Argon Group.

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In continuation of the determinations of viscosity already recorded,* measurements of the temperature variation for the five gases of the argon group have now been obtained. The apparatus used was of the same type as that described in the above papers, with certain modifications to render it suitable for working at different temperatures. Unfortunately, the method is only practicable for a somewhat limited range of temperature. On the one hand, the temperature must be lower than that at which the vapour pressure of mercury becomes appreciable, on account of the very high viscosity of the latter; on the other hand, it must not approach the solidifying point of mercury. At 100° C. the vapour-pressure of mercury is about 1/5 mm. This was judged to be as much as could be safely neglected, and observations were therefore taken at two temperatures only, viz., atmospheric temperature and the temperature of steam. However, although these limitations render observations over a large range impossible, they still allow interesting comparisons to be made of the temperature variations of the different gases. Incidentally, redeterminations of the ratios of the viscosities of the gases to that of air have also been obtained with an entirely new apparatus.

Apparatus.

Fig. 1 represents the apparatus in its modified form. The capillary tube was bent twice as shown in order to reduce the total length of the apparatus without seriously altering the time occupied by the mercury pellet P in descending. More than 100 cm. of capillary tubing was thus included, although the distance between the taps Y and Z was rather less than 50 cm. Two small bulbs B_1 and B_2 of about 1 c.c. each were introduced to serve as receptacles for the mercury pellet during the processes of exhausting and filling the apparatus. The total volume between the taps was about 6 c.c. A steam jacket 4 cm. in diameter covered as much as possible of the tubes between Y and Z, a few centimetres only projecting beyond the corks. The tubes passing through the corks were about 1 mm. internal diameter, so that their capacity represented a small fraction only of the whole. The steam jacket was clamped at its middle point and arranged on an axle perpendicular to its length, so that the apparatus could be inverted as desired. A thermometer was inserted for determining the atmospheric temperature only, the steam temperature being calculated from the barometric height.

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* 'Roy. Soc. Proc.,' A, vol. 83, pp. 265 and 516.

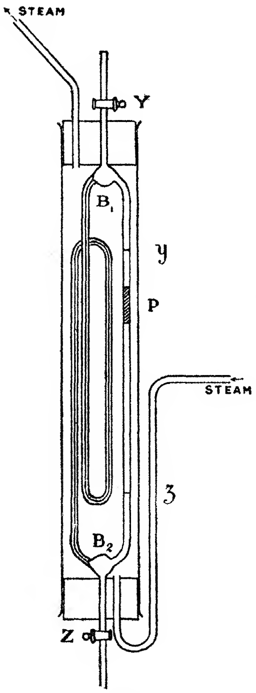

FIG. 1.

The auxiliary apparatus for exhausting and filling was precisely that which has been previously described, no alterations having been found necessary.

Theory of the Method.

It will be seen that the ratio of the viscosities of a gas at two different temperatures is approximately equal to the ratio of the times of fall of the mercury pellet between the marks y and z at those temperatures. Certain corrections, however, must be applied. In the first place, allowance must be made for the expansion of the glass. Meyer's transpiration formula as applied to this method has been shown to take the form:—

$$\eta = \frac{\pi R^4 pt}{8\,lv}\left(1+\frac{4\lambda}{R}\right),$$

where R = radius of capillary tube,
l = length of capillary tube,
p = difference of pressure below and above the mercury pellet,
v = volume between the symmetrically placed marks y and z,
t = time of fall of mercury between y and z,
λ = mean free path in the gas.

Of these quantities R, l, v, and p depend upon the expansion of the glass. $4\lambda/\mathrm{R}$ is a very small term whose variation in this respect is quite negligible. We may put p in the form mg/A where mg is the weight of the pellet and A is the cross-sectional area of the tube containing it. Hence

$$\eta = \mathrm{K} \cdot \frac{\mathrm{R}^4 t}{lv\mathrm{A}},$$

where K is a constant as regards temperature.

Let γ be the linear coefficient of expansion of glass, and θ the temperature difference which causes the viscosity to change from η_1 to η_2, and the time of fall from t_1 to t_2. Then

$$\frac{\eta_2}{\eta_1} = \frac{t_2}{t_1} \cdot \frac{(1+4\gamma\theta)}{(1+\gamma\theta)(1+3\gamma\theta)(1+2\gamma\theta)} = \frac{t_2}{t_1}(1-2\gamma\theta).$$

since $\gamma\theta$ is very small.

That is to say, the ratio of the viscosities is less than the ratio of the times in the ratio $(1-2\gamma\theta):1$. Taking $\gamma = 0{\cdot}000009$ and θ about 84° C., $2\gamma\theta$ becomes 0·0015, a correction which it is necessary to make.

Secondly, it is necessary to consider whether the variation in mean free path is appreciable. In cases where the pressure remains constant, there is a considerable alteration when the temperature rises from atmospheric temperature to 100° C. But in this case the density and not the pressure remains constant, and a calculation shows that under these circumstances the mean free path increases by only 6 per cent. over the temperature range referred to. Since the mean free path itself only enters the formula as a small correction, so small an alteration in its magnitude is quite negligible.

Consideration was also given to the question of the variation with temperature of the surface tension of mercury. As shown in my first paper* on this method, the unsymmetrical shape assumed by the mercury pellet in descending produces an effective reduction of driving pressure. For tubes of the size used in these experiments this reduction amounts to about 3 per cent. of the whole pressure difference, when the length of the mercury pellet is, as in this case, between 4 and 5 cm. The question is whether this capillary diminution will vary so much with temperature as to make appreciable the effect of its variation on the total driving pressure. The data with regard to the temperature variation of the surface tension of mercury are apparently not very reliable, but for the purpose of applying a small correction the decrease of surface tension for the rise of temperature from 15° to 100° C. may be taken as amounting to about 6 per cent. in the case where air is the superposed fluid. Upon this basis the effective increase of total driving pressure for the said range would be equal to 3 per cent. × 6 per cent. = 0·18 per cent. This correction is of the same order as that of errors liable to occur in the measurements; but it has not been applied, owing to the uncertainty of its applicability to cases where gases other than air are in contact with the mercury. It is true that corrections of the same order are applied, as, for instance, that due to the expansion of the glass; but these are perfectly definite and accurately known. It should be pointed out, however, that the values obtained for the temperature coefficients are probably slightly lower than the correct ones owing to this cause. This will be referred to later.

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* 'Roy. Soc. Proc.,' 1910, A, vol. 83, p. 265.

The necessity for the remaining correction appeared during test experiments with air. It was suspected that the exposed portion of the gas enclosed in the apparatus, *i.e.*, that part projecting through the corks, rendered the higher temperature virtually lower than that estimated. To test this point, further experiments were made with the tubes leading to the taps filled with mercury so as to exclude the air. It was then found that the mean time of fall at steam temperature was increased in the ratio 1·0028 : 1. Since it was not practicable to exclude the gas from the exposed region in this manner when dealing with the rare gases, the mean times of fall at the steam temperature have been increased in the above ratio for the purpose of calculating the temperature coefficients.

Method of Observation.

The apparatus, having been exhausted and then filled with the gas in question, was disconnected from the pump and allowed to stand until the thermometer indicated that the temperature had remained steady for a considerable time. In no case was the variation more than one or two fifths of a degree Centigrade during half-an-hour immediately preceding the commencement of an observation. The times of four falls of the mercury pellet—two in each direction—were then measured. In order to ensure that the whole apparatus was raised to the estimated temperature, steam was passed through the jacket for some 15 minutes before commencing the second set of observations. The passage of steam was, of course, continued throughout. Again four times of fall were measured, two in each direction. By taking the mean in each case the ratio of the viscosities of the gas at the two temperatures could be obtained after applying the corrections mentioned above. It was found that, as in previous determinations, non-uniformity of the tube containing the mercury pellet caused the times of fall in the two directions to differ slightly. Thus the time from y to z was consistently somewhat greater than that from z to y. However, by taking the mean of equal numbers of falls in the two directions, this effect can be eliminated.

Several determinations were first of all made with air, with very consistent results, the greatest variation in the calculated temperature coefficient being less than 1 per cent. The same mercury pellet was used throughout the whole final series of experiments. This made it possible not only to determine the temperature coefficient for each gas, but also to re-determine the relative values of the viscosities of the different gases.

Experimental Results.

The results of the four determinations made with air were as follows :—

$$\frac{\eta_{100}}{\eta_{15\cdot4}} = 1\cdot216, \qquad \frac{\eta_{99\cdot8}}{\eta_{15\cdot9}} = 1\cdot214,$$

$$\frac{\eta_{99\cdot7}}{\eta_{14\cdot5}} = 1\cdot219, \qquad \frac{\eta_{99\cdot9}}{\eta_{16\cdot4}} = 1\cdot212.$$

The corrections for the expansion of the glass and for the end error referred to above have been applied in calculating these ratios. The suffixes to η indicate the temperatures. The results indicate that temperature variations of about one-third of a degree are detectable.

In the cases of the rare gases the actual observations will be given.

1.—Helium.—

Times of fall, in seconds.

Temperature 13°·2 C.		Temperature 99°·7 C.	
y to *z*.	*z* to *y*.	*y* to *z*.	*z* to *y*.
126·0	125·4	150·8	149·2
126·0	125·2	150·6	149·4
Mean of all = 125·65 seconds.		Mean of all = 150·0 seconds.	

$$\frac{\eta_{99\cdot7}}{\eta_{13\cdot2}} = \frac{150\cdot0}{125\cdot65} \text{ approximately.}$$

Applying the necessary corrections,

$$\frac{\eta_{99\cdot7}}{\eta_{13\cdot2}} = 1\cdot195.$$

2. Neon.—

Times of fall, in seconds.

Temperature 13°·8 C.		Temperature 100° C.	
y to *z*.	*z* to *y*.	*y* to *z*.	*z* to *y*.
200·6	199·6	237·6	236·4
200·4	199·6	237·4	236·2
Mean of all = 200·1 seconds.		Mean of all = 236·9 seconds.	

$$\frac{\eta_{100}}{\eta^{13\cdot8}} = \frac{236\cdot9}{200\cdot1} \text{ approximately.}$$

Applying corrections,

$$\frac{\eta_{100}}{\eta_{13\cdot 8}} = 1\cdot 185.$$

3. Argon.—

Times of fall, in seconds.

Temperature 16°·0 C.		Temperature 99°·6 C.	
y to *z*.	*z* to *y*.	*y* to *z*.	*z* to *y*.
143·8	142·0	176·0	174·4
143·6	142·4	175·4	174·4
Mean of all = 142·95 seconds.		Mean of all = 175·05 seconds.	

$$\frac{\eta_{99\cdot 6}}{\eta_{16\cdot 0}} = \frac{175\cdot 05}{142\cdot 95} \text{ approximately.}$$

Applying corrections,

$$\frac{\eta_{99\cdot 6}}{\eta_{16\cdot 0}} = 1\cdot 226.$$

4. Krypton.—

Times of fall, in seconds.

Temperature 16°·3 C.		Temperature 100° C.	
y to *z*.	*z* to *y*.	*y* to *z*.	*z* to *y*.
161·0	159·8	200·2	198·4
160·4	160·0	199·8	199·2
Mean of all = 160·3 seconds.		Mean of all = 199·4 seconds.	

$$\frac{\eta_{100}}{\eta_{16\cdot 3}} = \frac{199\cdot 4}{160\cdot 3} \text{ approximately.}$$

Applying corrections,

$$\frac{\eta_{100}}{\eta_{16\cdot 3}} = 1\cdot 245.$$

5. Xenon.—

Times of fall, in seconds.

Temperature 15°·3 C.		Temperature 100°·1 C.	
y to *z*.	*z* to *y*.	*y* to *z*.	*z* to *y*.
145·6	145·2	185·4	184·2
146·0	144·6	185·2	184·2
Mean of all = 145·35 seconds.		Mean of all = 184·75 seconds.	

$$\frac{\eta_{100\cdot 1}}{\eta_{15\cdot 3}} = \frac{184\cdot 75}{145\cdot 35} \text{ approximately.}$$

Applying corrections,

$$\frac{\eta_{100\cdot 1}}{\eta_{15\cdot 3}} = 1\cdot 272.$$

The collected results are given in Table I.

Table I.

Gas.	Temperatures.	Ratio of viscosities.
	° C. ° C.	
Helium	99·7, 13·2	1·195
Neon	100·0, 13·8	1·185
Argon	99·6, 16·0	1·226
Krypton	100·0, 16·3	1·245
Xenon	100·1, 15·3	1·272

Further, by comparing the times of fall with that in air, the values of the ratio η/η_{Air}, shown in Table II, were obtained. In calculating these ratios, allowance has been made for the different slipping coefficients of the various gases, as described in my previous paper.

Table II.

Gas.	Temperature.	η/η_{Air}.
	° C.	
Helium	13·2	1·085
Neon	13·8	1·718
Argon	16·0	1·222
Krypton	16·3	1·362
Xenon	15·3	1·234

Treatment and Discussion of Results.

In order to make exact comparison possible in those cases where previous determinations have been made, it is necessary to assume a law of variation with temperature. It is, of course, not possible to deduce the law from the present measurements, since they only refer to two temperatures. For purposes of comparison, however, the law itself is not of the first importance, provided that the same temperature range is dealt with. As a first approximation we may therefore write

$$\eta_\theta = \eta_0(1+\beta\theta),$$

where η_θ and η_0 are the viscosities at temperatures θ and 0° C. respectively, and β is the coefficient of increase of viscosity with temperature. The ratios given in Table I enable us to calculate β for each of the gases.

The values of β for the four determinations made with air are 0·00266, 0·00267, 0·00266, and 0·00265—mean 0·00266.

The values of β for the rare gases are given in the second column of Table III. It will be noticed that with the exception of the drop from helium to neon, a rise in atomic weight is accompanied by an increase in the temperature coefficient of viscosity. Thus the latter is by no means proportional to the viscosity itself, since the alternations previously shown to affect the viscosity do not exhibit themselves.

A more usual method of treating the results is upon the basis of Sutherland's* formula—

$$\eta = \mathrm{K} \,.\, \mathrm{T}^{\frac{1}{2}}\Big/\left(1+\frac{\mathrm{C}}{\mathrm{T}}\right),$$

where T is the absolute temperature, and K and C constants for the gas, the latter depending on the attraction between the molecules. C can be calculated from a knowledge of the ratio of the viscosities of the gas at two different temperatures.

The equation may be written in the form—

$$\eta = \eta_0\left(\frac{\mathrm{T}}{\mathrm{T}_0}\right)^{\frac{3}{2}}\left(\frac{\mathrm{C}+\mathrm{T}_0}{\mathrm{C}+\mathrm{T}}\right),$$

where η_0 is the viscosity at the temperature T_0, *i.e.*, 0° C.

The values of C have been calculated by the use of the ratios in Table I alone. In order to obtain η_0, the absolute value for air obtained by the author, together with the ratios in Table II, has been used. These quantities occupy columns 3 and 4 in Table III.

Table III.

Gas.	$\beta \times 10^3$.	$\eta_0 \times 10^4$ (abs. units).	C.
Helium	2·32	1·879	70
Neon	2·21	2·981	56
Argon	2·83	2·102	142
Krypton	3·08	2·334	188
Xenon	3·39	2·107	252
Air	2·66	1·724	116

The probable error, having regard to the length of time measured, is about 1 per cent. in β, which is equivalent to about 3 per cent. in C.; thus, for example, in the case of helium, β probably lies between $2{\cdot}30 \times 10^{-3}$ and $2{\cdot}34 \times 10^{-3}$, and C between 68 and 72.

Comparisons with the results of previous observers may be made with respect to air, helium, and argon. In the case of air the value C = 116 obtained in the present measurements is about the average of those deduced from some of the more recent determinations. These values are:—

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* 'Phil. Mag.,' 1893, vol. 36, p. 507.

Rayleigh[*] 111·3, Sutherland[†] 113, Breitenbach[‡] 119·4, and Schultze[§] 121.

For helium, Rayleigh[||] found C = 72 as compared with 70, and for argon 150 as compared with 142.

Schultze's[¶] values are 80·3 and 169·9 for helium and argon respectively, but this was for a larger temperature range. If Schultze's observations for the range from atmospheric temperature to 100° C. are used for calculating C, it becomes 75 for helium and 156 for argon.

It will be seen that in both cases the values here recorded are somewhat lower than those of Rayleigh and Schultze. It is just possible that the discrepancies partly arise from the cause previously referred to, viz., the slight increase of total driving pressure with rise in temperature, brought about by the diminution of the surface tension of the mercury. For reasons given earlier, the magnitude of this effect was considered too uncertain to justify application. If, however, this were done, the value of β would be increased by about 1 per cent. and that of C about 3 per cent. This would bring up the values of the latter according to the present measurement to 72 in the case of helium and 146 for argon. This still leaves a considerable divergence between Schultze's values and the present ones; but if the comparative difficulties attending the measurement of temperature coefficients over small temperature ranges are taken into consideration, this is not surprising. Similar differences in the value of C obtained by independent observers usually exhibit themselves, as, for example, the variety of values in the case of air quoted above.

Returning to a consideration of the relative values of C for the rare gases, it is surprising to find that it is higher for helium than for neon. According to Sutherland the introduction of C is rendered necessary because gases are not perfect. For a perfect gas C would be zero and the viscosity would vary as the square root of the absolute temperature. Now it is certain that the critical and liquefying points of helium are lower than those of neon; hence, it would be natural to suppose that C_{He} would be nearer zero than C_{Ne}. This, apparently, is not the case, and it seems that in the temperature range considered neon is to be regarded as the nearest approach to a perfect gas known. In the case of the other gases we find what would be expected, namely, that C is high or low according as the critical and liquefying points are high and low. In this connection it is interesting to note that a simple relation exists between the value of C and the critical temperature. This will be obvious from the following table, which refers to those of the rare gases whose critical temperatures are known:—

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[*] 'Roy. Soc. Proc.,' A, 1900, vol. 67, p. 137.

[†] 'Phil. Mag.,' 1893, vol. 36, p. 507.

[‡] 'Wied. Ann.,' 1899, vol. 67, p. 813.

[§] 'Ann. der Physik,' 1901, vol. 5, p. 140.

[||] 'Roy. Soc. Proc.,' A, 1900, vol. 67, p. 137.

[¶] 'Ann. der Physik,' 1901, vol. 6, p. 302, and 1901, vol. 5, p. 140.

Table IV.

Gas.	C.	T_c (abs.).	T_c/C.
Argon	142	155·6	1·10
Krypton	188	210·5	1·12
Xenon	252	288	1·14

Thus it appears that the constant C is sensibly proportional to the critical temperature. It must be pointed out that this would certainly not apply to helium, where the value C = 70 is far larger than the probable critical temperature. Supposing, however, that it does apply to neon, an assumption possibly justifiable in view of the abnormal behaviour of helium referred to above, we should expect the critical temperature of neon to be about 63° absolute.

The existence of the above relation led the author to test its applicability to gases other than those of the argon group. The material available as regards viscosity measurements is very limited, but values are obtainable for hydrogen, oxygen, nitrogen, ethylene, nitrous oxide, and carbon dioxide. In the latter case the values of C obtained by Sutherland and Breitenbach differ considerably—277 and 240 respectively; hence the mean has been taken. For the first three gases the values recorded recently by Schmitt* have been used; the values for ethylene and nitrous oxide are taken from Landolt and Börnstein's tables. The results are as follows:—

Table V.

Gas.	C.	T_c.	T_c/C.
Hydrogen	83	37	0·45
Nitrogen	113	127	1·12
Oxygen	138	154	1·12
Carbon dioxide	259	304	1·17
Ethylene	249	283·6	1·14
Nitrous oxide	260·4	309·9	1·19

Here, again, there is an exception, viz., hydrogen; but, for the other gases, not only is the ratio T_c/C nearly constant, but the constant is the same as for the rare gases. It is to be expected that C, which depends on the mass and dimensions of the molecules, would be in some way connected with the critical temperature; and should the above simple relation be found to be practically universal, considerable additional importance attaches to Sutherland's constant.

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* 'Ann. der Physik,' 1909, vol. 30, p. 398.

I have also made use of the temperature coefficients to re-determine the ratio η/η_{Air} for comparison with the results recorded in my last paper. The values given in Table II are for rather higher temperatures than the earlier determinations. Upon reduction to the same temperatures we obtain results recorded below:—

Table VI.

Gas.	Temperature.	η/η_{Air}.	
		Original value.	Present value.
	° C.		
Helium	9 ·8	1 ·086	1 ·086
Neon	10 ·1	1 ·721	1 ·721
Argon	12 ·3	1 ·221	1 ·221
Krypton	10 ·6	1 ·361	1 ·359
Xenon	10 ·9	1 ·234	1 ·231

The agreement is remarkably close, especially in view of the fact that the apparatus used in the two cases was entirely different. This suggests that, at any rate as regards comparative measurements, the method is thoroughly reliable.

The values of the viscosity for the various gases are given in absolute C.G.S. units in Table VII. These are based upon the absolute values for air previously obtained by the author.

Table VII.

Gas.	Temperature.	$\eta \times 10^4$.
	° C.	
Helium	13 ·2	1 ·942
	99 ·7	2 ·322
Neon	13 ·8	3 ·080
	100 ·0	3 ·652
Argon	16 ·0	2 ·204
	99 ·6	2 ·702
Krypton	16 ·3	2 ·459
	100 ·0	3 ·063
Xenon	15 ·3	2 ·222
	100 ·1	2 ·827
Air	15 ·9	1 ·803
	99 ·8	2 ·189

Re-calculation of Relative Molecular Dimensions.

Sutherland, in the paper previously referred to, bases his extension of the simple form of the kinetic theory upon the idea that the mutual attractions between the molecules make collisions more frequent than would be the case with forceless molecules. He shows that this is equivalent to a virtual increase in the cross-sectional area of the molecule, and deduces the important result that the molecules may be regarded as forceless, and hence the simple form of the kinetic theory as valid, provided that the true cross-sectional area of the molecule is imagined increased in the ratio $(1+C/T):1$. In every case where C is known, the true molecular dimensions can be deduced from the virtual ones by the application of this principle. Thus, if a' is the virtual radius, *i.e.*, the value calculated on the simple theory, and a the true radius,

$$a = a' \Big/ \left(1+\frac{C}{T}\right)^{\frac{1}{2}},$$

and the true volume can also be deduced.

I have applied this correction to the relative molecular dimensions recorded in my previous paper. In the following table helium is taken as a standard throughout:—

Table VIII.

Gas.	Relative radius.		Relative volume.		Relative atomic density.	
	New.	Old.	New.	Old.	New.	Old.
Helium	1·00	1·00	1·00	1·00	1·00	1·00
Neon	1·21	1·19	1·79	1·69	2·83	2·99
Argon	1·53	1·68	3·59	4·74	2·81	2·12
Krypton	1·65	1·91	4·53	6·98	4·63	3·00
Xenon	1·83	2·25	6·11	11·37	5·40	2·90

The alterations effected by this correction are very considerable, owing to the large differences in C. I have been unable, up to the present, to discover any simple relations between the various radii and volumes. The size of the atom apparently increases with increasing atomic mass, and, with the exception of the step between neon and argon, there is a general tendency for the density to increase with size. It is, perhaps, also worthy of note that the densities of the atoms of argon and neon are practically identical.

I wish again to express my gratitude to Sir William Ramsay for his kindness in continuing the loan of specimens of these valuable gases for the purposes of these measurements. To Prof. Trouton and Prof. Porter my thanks are also due for much helpful advice.